

**PROCEEDINGS**  
OF THE  
**NATIONAL ACADEMY OF SCIENCES**  
**INDIA**  
**1948**

---

PART III]

SECTION A

[Vol. 17

---

**CONTENTS**

	Page
1. A Note on High Frequency Current Density in a Hollow Cylindrical Conductor <i>By Santi Ram Mukherjee</i>	69
2. Preparation and Study of Thorium Borate Jellies <i>By S. P. Mushran</i>	73
3. Intensity Variations of Radio Signals and their bearings on Diversity Reception <i>By Ram Neti Singh</i>	83
4. Studies in the nature of Hydrated Ferric Oxide Part II Adsorption of various ions by the Hydrated Oxide in Acidic, Alkline and Neutral Media <i>By Arun K. Dey &amp; Satyeshwar Ghosh</i>	93

ALLAHABAD

**PUBLISHED BY THE COUNCIL**

Price Rs. 5 (India) : Rs. 5/8 (Foreign)

**PROCEEDINGS**  
OF THE  
**NATIONAL ACADEMY OF SCIENCES**  
**INDIA**  
**1948**

---

PART III]

SECTION A

[ Vol. 17

---

CONTENTS

	Page
1. A Note on High Frequency Current Density in a Hollow Cylindrical Conductor <i>By Santi Ram Mukherjee</i>	69
2. Preparation and Study of Thorium Borate Jellies <i>By S. P. Mushran</i>	73
3. Intensity Variations of Radio Signals and their bearings on Diversity Reception <i>By Ram Neti Singh</i>	83
4. Studies in the nature of Hydrated Ferric Oxide Part II Adsorption of various ions by the Hydrated Oxide in Acidic, Alkline and Neutral Media <i>By Arun K. Dey &amp; Satyeshwar Ghosh</i>	93

ALLAHABAD

**PUBLISHED BY THE COUNCIL**

Price Rs. 5 (India) : Rs. 5/8 (Foreign)

PROCEEDINGS  
OF THE  
**NATIONAL ACADEMY OF SCIENCES  
INDIA**  
1948

PART III]

SECTION A

[Vol. 17

**A NOTE ON HIGH FREQUENCY CURRENT DENSITY  
IN A HOLLOW CYLINDRICAL CONDUCTOR.**

By

SANTI RAM MUKHERJEE.

ENGINEERING COLLEGE, BANARAS HINDU UNIVERSITY.

Received on April 2, 1948.

Hollow cylindrical conductors have lately gained very wide application in Radio Engineering. Due to their non-radiating properties, they are conveniently used in connection with ultra-short and micro-wave transmission lines, wave-guides, etc., particularly for radar and television purposes. It is often found necessary to know the current density along the radius of such a conductor, specially to detect the formation of stationary waves along the cross-section of the tube. The current-density for steady sinusoidal current (1) can be calculated by Bessel functions, and in the present communication, the solution has been obtained for varying high frequency current following through the conductor. For the purpose of relaxed oscillations, a solution has also been obtained for linear variation of current with time.

If  $\mu$  be the permeability,  $\rho$  the resistivity of the material of the cylindrical conductor, the value of current density  $g$  at any radius  $r$  can be obtained from the differential-equation,

$$\frac{\partial^2 g}{\partial r^2} + \frac{1}{r} \frac{\partial g}{\partial r} - \frac{4\pi\mu}{\rho} \frac{\partial g}{\partial t} = 0 \quad \dots (1)$$

For steady sinuisoidal high frequency current, it may be assumed that  $\frac{\partial g}{\partial t} = j\omega g$ , where  $\omega$  is the pulsantance of the current. Then the solution of (1) is given by

$$g = \{A I_0(kr\sqrt{j}) + BK_0(kr\sqrt{j})\} (\cos \omega t \times j \sin \omega t) \quad \dots (2)$$

Where  $I_0$  and  $K_0$  represent ber-bei and ker-kei functions respectively.

In case the high frequency current is varying, the solution of equation (1) may be obtained as shown below.

Let  $g = g_1 g_2$  where  $g_1 = f_1(r)$  and  $g_2 = f_2(t)$ .

$$\text{Then from (1), } g_2 \left( \frac{d^2 g_1}{dr^2} + \frac{1}{r} \frac{dg_1}{dr} \right) - A_1 g_1 \frac{dg_2}{dt} = 0, \quad \text{where } A_1 = \frac{4\pi\mu}{\rho}$$

$$\text{or } \frac{1}{g_1} \left( \frac{d^2 g_1}{dr^2} + \frac{1}{r} \frac{dg_1}{dr} \right) - \frac{A_1}{g_2} \frac{dg_2}{dt} = 0.$$

This is satisfied if we write.

$$\frac{d^2 g_1}{dr^2} + \frac{1}{r} \frac{dg_1}{dr} - k g_1 = 0 \quad \text{and} \quad \frac{dg_2}{dt} = \frac{k}{A_1} g_2, \quad k \text{ being an arbitrary constant.}$$

$$\text{Now} \quad \frac{d^2 g_1}{dr^2} + \frac{1}{r} \frac{dg_1}{dr} - k g_1 = 0. \quad \dots (3)$$

Will give rise to  $I_0$  and  $K_0$  functions.

$$\text{From } \frac{dg_2}{dt} = \frac{k}{A_1} g_2 = (-\alpha + j\bar{\omega}) g_2 \quad \text{where } \frac{k}{A_1} = -\alpha + j\bar{\omega} \quad \dots (4)$$

$$\text{We get } g_2 = c_1 e^{-\alpha t} (\cos \bar{\omega} t + j \sin \bar{\omega} t) \quad \dots (5)$$

The value of  $g$  can thus be calculated from (3) and (5). It may be observed that in particular, by putting  $\alpha = 0$  in (4), we obtain the case of steady sinusoidal high frequency current already solved.

For linear variation of current density with time, let  $g = g_1 + g_2$  where  $\bar{g}_1$  is a function of  $r$  only and  $\bar{g}_2$  a function of  $t$  only.

Substituting this value of  $g$  in (1) we get

$$\frac{d^2 \bar{g}_1}{dr^2} + \frac{1}{r} \frac{d\bar{g}_1}{dr} - A_1 \frac{d\bar{g}_2}{dt} = 0. \quad \dots (6)$$

This is possible when

$$\frac{d^2 \bar{g}_1}{dr^2} + \frac{1}{r} \frac{d\bar{g}_1}{dr} = 4k_1 \quad (7), k_1 \text{ being an arbitrary constant}$$

$$\text{and } \frac{d\bar{g}_2}{dt} = \frac{4k_1}{A_1}$$

$$\text{or } \bar{g} = \frac{4k_1}{A_1} t + c_3 \quad (8), c_3 \text{ being an arbitrary constant.}$$

$$\text{From (7) } r \frac{d^2 \bar{g}_2}{dr^2} + \frac{d\bar{g}_1}{dr} = 4k_1 r$$

$$\text{or } r \frac{d\bar{g}_1}{dr} = 2k_1 r^2 + c_2, \quad c_2 \text{ being an arbitrary const.}$$

$$\text{or } \frac{d\bar{g}_1}{dr} = 2k_1 r + \frac{c_2}{r}$$

$$\text{or } \bar{g}_1 = k_1 r^2 + c_2 \log r \quad (9)$$

Thus combining (8) and (9) we get

$$g = \bar{g}_1 + \bar{g}_2 = k_1 r^2 + \frac{4k_1}{A_1} t + c_2 \log r + c_3.$$

Fuller discussion of the problem will be given in later publication. The author has pleasure to record his grateful thanks to Dr. S. S. Banerjee for suggesting the above problem and helpful discussions.

*Reference.*

- (1) A. G. Warren, "*Mathematics Applied to Electrical Engineering*" p. 243. (Chapman and Hall Limited, 1939).

# PREPARATION AND STUDY OF THORIUM BORATE JELLIES

By

S. P. MUSHRAN M.Sc., D. PHIL.

(CHEMICAL LABORATORY, THE UNIVERSITY, ALLAHABAD)

Received on August 12, 1948

## ABSTRACT

(1) Thorium borate jellies have been prepared and studied. The jellies were obtained by the slow coagulation of a purified sol of thorium borate having the composition  $4\text{ThO}_2 \cdot \text{Th}_3(\text{BO}_3)_4$ , obtained by dispersing freshly precipitated thorium borate in excess thorium nitrate, by electrolytes like potassium chloride and potassium sulphate.

(2) The sol-gel transformation of thorium borate has been investigated. It has been shown that the time of gelation  $\theta$  is related to the concentration ' $c$ ' of the coagulating electrolyte as  $\log S = \log R + P \log c$  where  $R$  and  $P$  are constants and  $S = 1/\theta$ .

(3) The influence of temperature on the time of setting of the jellies has been studied. It is observed that the jellies set more readily at higher temperatures than at low. The jellies are not formed above  $50^\circ\text{C}$ .

(4) The jellies are thixotropic in nature. The study of their thixotropic behaviour shows that the original time of setting of the jellies is always greater than the thixotropic time of setting. On repeated shakes the jellies lose their property of developing hydration and ultimately break up.

(5) The influence of 20% glucose and glycerine on the time of setting of the jellies has been investigated. It has been observed that glucose and glycerine exert markedly peptising influence on thorium borate sol and in their presence the original time of setting is increased.

(6) It has been shown that the minimum amount of electrolyte necessary to give a jelly of the sol of thorium borate is always greater than that required to coagulate it. The gelation and the coagulation points of thorium borate sol are thus two distinct points.

In some of the previous publications from these laboratories<sup>1</sup> the conditions of formation of thorium phosphate, arsenate, molybdate and tungstate jellies have been described. No attempt appears to

have been made to prepare the jellies of thorium borate. Berzelius<sup>2</sup> reported that boric acid precipitates white flocculent thorium borate when added to a solution of a salt of that element. Guertler<sup>3</sup> could not prepare thorium borate by fusing thoria with boric oxide on account of the very sparing solubility of the thoria. Karl<sup>4</sup> has discussed the composition of the amorphous white precipitate obtained by treating an aqueous solution of thorium nitrate with a hot solution of borax and showed that the composition corresponded to thorium orthoborate,  $\text{Th}_3(\text{BO}_3)_4$ . It has been now observed that the white precipitate of thorium borate obtained on adding a hot concentrated solution to thorium nitrate solution, can be made to dissolve, on vigorous shaking in presence of an excess of the latter. In this way a considerable amount of thorium borate can be made to disperse in thorium nitrate. If this mixture be dialysed until nearly free from all electrolytes, a clear colourless sol of thorium borate is obtained which can be shown to be positively charged by the cataphoretic method. It is easily coagulated with electrolytes like potassium chloride and potassium sulphate and when suitable concentrations of the coagulating electrolytes are used the sol sets to beautiful transparent jellies. In a note Mushran<sup>5</sup> has briefly described the conditions of preparation of this hydrogel and in this paper the details of the preparation and various properties of the gel have been investigated.

#### EXPERIMENTAL

A sol of thorium borate was prepared allowing a hot 20 percent solution of borax to run slowly into 75 c.c. of 10 percent thorium nitrate solution until the precipitate of thorium borate scarcely dissolved in thorium nitrate on vigorous shaking. The mixture was purified by dialysis, for eight days, at room temperature (30°C).

#### COMPOSITION OF THE SOL

The amount of thorium in a known volume of the sol was estimated by the use of the reagent cupferron. (Baudisch, Chem. Ztg., 33, 1298 (1909).) The amount of borate in the combined state with thorium was found by coagulating a known amount of the sol cataphoretically, the coagulum was collected and washed and estimated for

boric acid by the usual method (Clowes and Coleman 1938 page 418). The combined thorium corresponding to this amount of borate was calculated on the assumption that the thorium borate is  $\text{Th}_3(\text{BO}_3)_4$ . The rest of the thorium is present as hydrated thorium oxide. From the ratio of the free to the combined thorium, the empirical formula of the sol was calculated. An analysis is presented in Table I.

TABLE I

Per litre:

Total Thorium (Th)	...	...	18.0200 g
Combined Borate ( $\text{BO}_3$ )	...	...	2.6054
Combined Thorium (Th)	...	...	7.7112
Free Thorium (Th)	...	...	10.3088
Empirical Formula	...	...	$4\text{ThO}_2 \cdot \text{Th}_3(\text{BO}_3)_4$

When this sol was coagulated with N KCl and N/5  $\text{K}_2\text{SO}_4$  it gave beautiful transparent jellies. The influence of the variation of the concentration of the coagulating electrolyte on the time of the setting of the gel is shown in Table II.

TABLE II

Amount of sol taken = 2 c.c. Total volume = 3 c.c. Temp =  $30^\circ\text{C}$

Amount of N KCl (c.c.)	Time of setting (mins)
1.00	4
0.80	8
0.60	12
0.40	20
0.20	52

Amount of N/5 $\text{K}_2\text{SO}_4$ (c.c.)	Time of setting (mins)
0.28	2
0.26	4



0.24	7
0.22	10
0.20	15
0.18	20

*Influence of Temperature*

The influence of temperature on the time of setting of the jellies has been investigated. The results are recorded in Table III.

TABLE III

Volume of sol = 2 c.c.

Total volume = 3 c.c.

N KCl (c.c.)	Time of setting (mins)				
	25°	30°	40°	50°	60°
1.00	7	4	3	1	No Jelly
0.80	10	8	5	3	„
0.60	16	12	7	4	„
0.40	24	20	15	7	„
0.20	65	52	42	26	„
N/5 K <sub>2</sub> SO <sub>4</sub>					
(c.c.)					
0.28	5	2	Instantaneous Loose		No Jelly
			Jelly		
0.26	8	4	„	„	„
0.24	9	7	4	1	„
0.22	12	10	7	4	„
0.20	17	15	12	6	„
0.18	23	20	16	10	„

*Influence of Glucose and Glycerine*

The influence of glucose and glycerine on the time of setting of the jellies have also been investigated. The results are tabulated in Table IV.

TABLE IV

Influence of Glucose 20%		
Volume of sol = 2 c.c. Glucose 20% (c.c.)	Total volume = 3 c.c. Time of setting (mins)	Temp = 30°C
	0.20 c.c. N KCl	0.18 c.c. N/5 K <sub>2</sub> SO <sub>4</sub>
0.0	52	20
0.2	60	25
0.4	70	32
0.6	82	43
0.8	104	56

Influence of Glycerine		
Volume of sol = 2 c.c. Glycerine (c.c.)	Total volume = 3 c.c. Time of setting (mins)	Temp = 30°C
	0.20 c.c. N KCl	0.18 c.c. N/5 K <sub>2</sub> SO <sub>4</sub>
0.0	52	20
0.2	58	23
0.4	65	29
0.6	76	41
0.8	91	54

## THIXOTROPIC BEHAVIOUR

It has been observed that on vigorous shaking the jellies assume a liquid form, and the viscous liquid so obtained again sets to a jelly on standing and the process could be repeated several times. The jellies are therefore thixotropic in nature. The thixotropic behaviour

of the jellies has been investigated. The set jelly was vigorously shaken for about one minute to ensure complete transformation to the sol form, and the time it took to set again was noted. The results are tabulated in Table V.

TABLE V

Volume of sol = 2 c.c.	Total volume = 3 c.c.	Temp = 30°C
Time of setting (mins)		
	0.20 c.c. N KCl	0.18 c.c. N/5 K <sub>2</sub> SO <sub>4</sub>
Original setting	52	20
After 1st shake	34	16
„ 2nd „	25	14
„ 3rd „	20	6
„ 4th „	12	2
„ 5th „	5	Breaks
„ 6th „	Breaks	Breaks

*Relation between the Coagulation and the Gelation Points*

The relation between the coagulation and the gelation points of the positively charged thorium borate sol has also been investigated. Different amount of sols were mixed with 0.20 c.c. N KCl and 0.18 c.c. N K<sub>2</sub>SO<sub>4</sub> solutions, the total volume was kept 3 c.c. in each case, and the minimum amounts of electrolytes necessary to coagulate the sol and to give the jelly in 30 minutes were recorded. The results are tabulated in Table VI.

TABLE VI

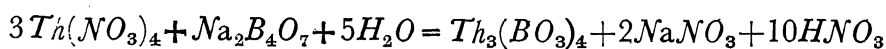
Electrolyte: N KCl		
Volume of sol (c.c.)	Gelation Point (c.c.)	Coagulation Point (c.c.)
1.0	0.18	0.10
1.5	0.24	0.14
2.0	0.30	0.18
2.5	0.38	0.25

Electrolyte: N/5  $K_2SO_4$ 

1.0	0.06	0.04
1.5	1.12	0.07
2.0	0.16	0.10
2.6	0.21	0.15

## DISCUSSION

According to Karl (loc. cit.) when a hot concentrated solution of borax is added to thorium nitrate solution a white precipitate of thorium orthoborate is obtained according to the following equation:



The insoluble thorium borate in presence of an excess of thorium nitrate gets peptised by the adsorption of thorium, hydrogen and other positively charged ions and a positively charged sol of thorium borate is obtained. The sol investigated in this paper has the composition  $4ThO_2 \cdot Th_3(BO_3)_4$ , showing that it contains an appreciable amount of thorium borate. If this sol without dialysis is coagulated with strong concentrations of coagulating electrolytes like potassium chloride or potassium sulphate, the coagulum obtained is a white opaque heavy mass which on allowing to stand settles down as a precipitate. However if the sol is purified by dialysis for a few days and then coagulated by  $KCl$  or  $K_2SO_4$  the coagulum obtained is gelatinous and with suitable concentrations of the coagulating electrolytes gives rise to clear, transparent and stable jellies.

In a paper Dube and Prakash<sup>6</sup> have studied the influence of the concentration of various coagulating electrolytes on the time of setting of various inorganic jellies. According to them the time of setting  $\theta$  is related to the concentration 'c' of the electrolyte as  $\log S = \log R + P \log c$  where  $R$  and  $P$  are constants and  $S = 1/\theta$ . It is evident that if the kinetics of the sol-gel transformation of thorium borate is represented by the above expression a straight line should be obtained on plotting the logarithm of concentration against the logarithm of the inverse of the time of setting of the gels. On plotting  $\log S$  against  $\log c$  from

the results recorded in Table I it is observed that straight lines are obtained. The results in general therefore follow the expression given by Dube and Prakash.

The influence of temperature on the time of setting of thorium borate jellies has been investigated. A perusal of Table III shows that the jellies set more readily at higher temperatures than at low. The jellies are not formed above  $50^{\circ}$ . In a paper Prakash and Dhar<sup>7</sup> have studied the influence of temperature on the coagulation of several sols and have shown that smaller quantities of electrolytes are required to coagulate at  $60^{\circ}$  than the amounts required for coagulation at  $30^{\circ}$ . On the basis of the above it is highly probable that as the temperature is raised the rate of coagulation and consequently the hydration of thorium borate sol is more rapidly developed and the jellies are more readily obtained. Also at higher temperatures thorium borate is partly hydrolysed to thorium hydroxide which has a great tendency to develop hydration and hence the setting time decreases with the increase of temperature.

In table IV are recorded the results of the influence of 20% glucose and glycerine on the time of setting of thorium borate jellies. It is easily seen that the time of setting is markedly increased by the addition of these substances to the gel forming mixtures. It is well known that glucose and glycerine are strong peptising agents and it is highly probable that in their presence thorium borate is further peptised and thus the the time of setting is greatly increased.

The thixotropic behaviour of thorium molybdate, phosphate and arsenate jellies have been investigated in a paper by Prakash and Biswas<sup>8</sup>. The thorium borate jellies investigated in this paper are also thixotropic and a perusal of Table V will show that the original time of setting of the jellies are much greater than the thixotropic time of setting. On shaking the structurally imbibed liquid of the jelly is set free forming a dispersion medium for the jelly forming elements and the jellies are transformed into the sol state. On standing the structure is again developed and the gel is again formed. On

repeated shakes the jelly loses its property of developing hydration and ultimately breaks up.

An attempt has also been made to investigate the relation between the coagulation and gelation points of the jelly forming thorium borate sol. From the results recorded in Table VI it is evident that more of the electrolytes are necessary to give the jelly of the sol in 30 minutes than to coagulate it. The results are in conformity with those obtained by Gessner<sup>9</sup>, Bhatia and Ghosh<sup>10</sup> and Prakash<sup>11</sup> for various jelly forming sols. It appears that there is always a fixed amount of electrolyte necessary to give a stable jelly in a definite time. Any amount lesser than this leads to coagulation without allowing the coagulated particles to develop hydration and any amount greater than this gives a gelatinous precipitate.

My thanks are due to Dr. Satya Prakash for his very kind interest in this work.

#### References

1. Prakash and Dhar. *J. Indian Chem. Soc.* **7**, 367 (1930).
2. Berzelius. *Pogg. Ann.* **16**, 385 (1829)
3. Guertler. *Z. anorg. Chem.*, **40**, 232 (1904)
4. Karl. *Z. anorg. Chem.*, **68**, 57 (1910)
5. Mushran. *Nature*, **158**, 95 (1946)
6. Dube and Prakash. *Z. anorg. Chem.* **208**, 163 (1932)
7. Dhar and Prakash. *J. Phys. Chem.*, **34**, 954 (1930)
8. Prakash and Biswas. *J. Indian Chem. Soc.*, **8**, 549 (1931)
9. Gessner. *Koll. Chem. Beih.* **19**, 213 (1924)
10. Bhatia and Ghosh. *J. Indian Chem. Soc.* **7**, 687 (1930)
11. Prakash. *J. Indian Chem. Soc.* **9**, 137 (1932)

# **INTENSITY VARIATIONS OF RADIO SIGNALS AND THEIR BEARING ON DIVERSITY RECEPTION**

By

RAM NETI SINGH M. Sc.

UNIVERSITY RESEARCH SCHOLAR

Engineering College, Banaras Hindu University.

(Communicated by Professor A. C. Banerji, F. N. I. T. N.A. Sc.,)

24th August 1948.

## **1. INTRODUCTION.**

Appleton and Barnett (1) showed the existence of ionized layer in the upper atmosphere by their experiments on fading of radio signals as early as in 1925. Since then various investigators (2-5) became interested with the study of signal intensity received at a distance from the transmitter, particularly for the purpose of investigating the conditions of the ionosphere suitable for establishment of radio communications between two stations.

In these experiments medium waves were generally employed and observations were taken mostly in the presence of ground wave. In case of short waves, however, the fading of signals has been recorded outside the reach of ground wave, and the nature of variations of intensity of the received signal has been found to be rather irregular. Such variations have been attributed to random scattering of signal from diffracting centres in the ionosphere by Ratcliffe and Pawsey (3). Observations on short wave signals had shown that variations of intensity were often very quick and sometimes possessing periodic characteristics. Satisfactory explanations for various types of fading observed, particularly for short distance transmissions however, appear to be still very inadequate.

For reasons stated above it was considered useful to make some detailed investigations of the fading of short wave signals and a few

preliminary reports on such observations have already been published from this laboratory (6,7). The present communication is intended to exhibit the occurrence of various types of fading observed for short wave transmissions on wavelengths of 19 to 41-metre-bands from Delhi and also from foreign and other Indian stations. In order to study the finer details of the intensity variations of received signals, continuous records of the observations were made on much extended time scale. The various types of fading have been conveniently divided into three main groups according to their mode of formation, namely,

- (1) Random variation of peaky type,
- (2) Slow and comparatively regular or quasi-periodic variations, and
- (3) Regular variations of periodic nature.

The various types of fading have been accounted for by the different conditions of the ionosphere at the time of observations. It has been further shown that such experimental investigations on fading of signals are useful for the development and understanding of the principle of diversity reception of radio signals. Theoretical considerations and experimental observations show that it is possible to minimize the fading of received signals from a distant transmitter by space-diversity reception with vertically spaced aerials situated at a much smaller distance between them compared to the distance required in case of horizontally spaced aerials usually used for such reception.

## 2. THEORETICAL CONSIDERATIONS

It is generally assumed that the variations of intensities of radio signals at a distance from the transmitter are of random nature. Some investigators (5), however, have reported that this assumption does not hold good on many occasions particularly when the receiver is at a large distance from the transmitter. This inconsistency between the observed and the theoretically assumed variations indicates that during the period of observations there must have been occasions



when the variation of the intensity of signal was less random or it acquired some characteristic of periodic nature.

For the above considerations the observations were recorded on a much extended time scale as stated before and all the three types of fading mentioned in the previous section were obtained. These types of fading have been found to continue sometimes for a fairly long time, and also the patterns of fading have been observed changing with time.

The various types of fading and their change may be attributed to single, double or multiple spot reflections at the ionosphere. For example, the peaky random type of fading will be observed when there is only one spot reflection from the ionosphere with no other reflection either from the same or any other layer. Second type of fading namely quasiperiodic or slow random, is due to more than one spot reflection either from one layer or from two different layers in the ionosphere. Evidently in such cases the resultant intensity of the received signal at any moment will depend on the vector sum of the independent components arriving from different spots of the ionosphere. Thus at an instant when the strength of the signal due to one component tends to increase, the other component may tend to decrease and thereby the resultant intensity may remain comparatively constant. This reduces the peaky nature of the received signal and gives rise to slow random pattern. The above principle of reduction of fading is utilised in space diversity reception by using more than one aerial system as described in the subsequent section.

The third or periodic type of variation of signal intensity may be attributed to two different causes. One is due to interference fringes caused either by single and double reflections from the same layer or by two single reflections from two different layers, when one or both the layers have slow vertical movement. The other is due to magnetoionic splitting of the incident wave at the ionosphere when the electronic density in the ionospheric layer is decreased to a value corresponding to maximum usable frequency for the wave

used for transmission as suggested by Appleton and Beynon (8). Both these types of fading have been observed by us and the records of these are shown in the following section.

### 3. EXPERIMENTAL ARRANGEMENT

A 5-valve superhet receiver was built without automatic volume control system and was employed for visual observations of the received signal intensities. A sensitive and low resistance moving coil mirror galvanometer was connected in the diode circuit of the second detector of the receiver for observing the fading of received signals. Usually the observations were made at interval of 5 seconds and the scale deflections could be measured up to 50 cms.

In order to have a continuous record of the observations an automatic recorder was constructed. The arrangement consisted of a 7-valve superhet commercial receiver, the *a. v. c.* of which was made inoperative. The rectified voltage developed across the resistance in the diode circuit of the second detector of the receiver was amplified by means of a two stage direct coupled amplifier. The amplified voltage so obtained was applied to a recording galvanometer which had a writing pen attached to it. The initial plate current in the galvanometer was balanced by means of an external battery of about 30 volts. The writing pen moved in a vertical plane over which 4-inch wide paper for recording was run by a self-governed electric motor. The vertical speed of the paper could be varied and the deflections of the recording galvanometer were calibrated for field intensities.

### 4. OBSERVATIONS

Typical records of the three types of fading, mentioned in the previous section, are shown in figs. 1-4. For convenience, the description of the diagrams is summarised in table I below. In order to check the conditions for different types of fading patterns, the electronic densities in  $F_2$ -layer at the time of observations, were calculated from the ionospheric data supplied by the Research Department All India Radio, Delhi, and they are included in the last column of the

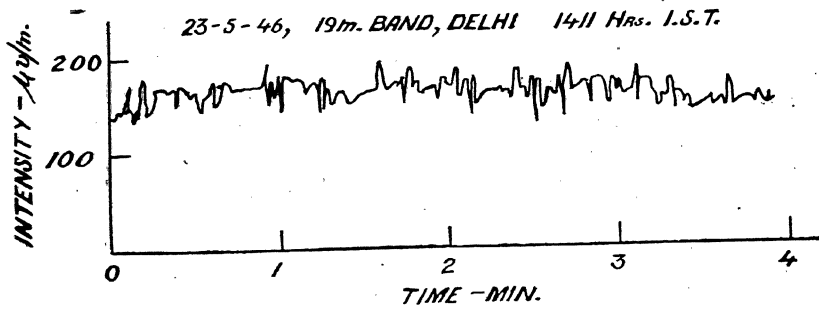


Fig. 1

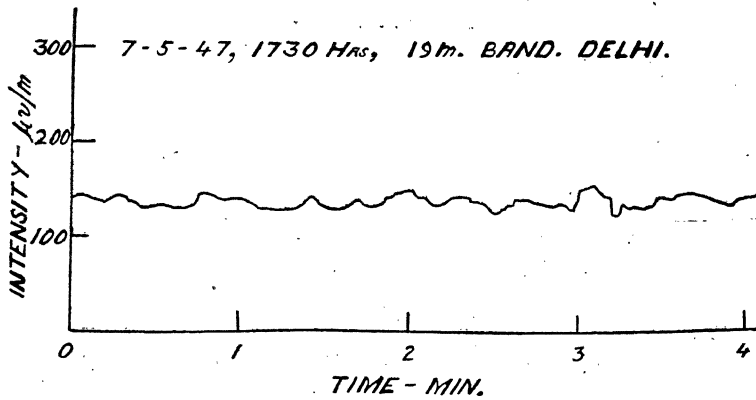


Fig. 2

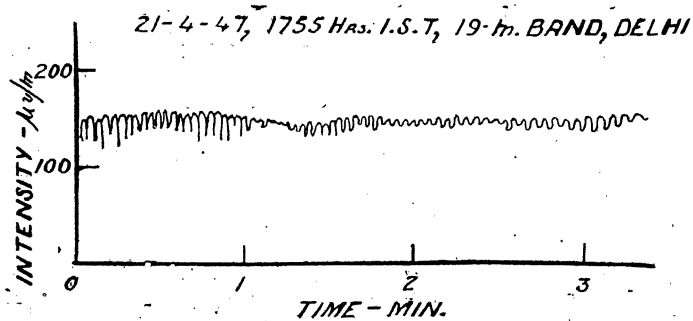


Fig. 3

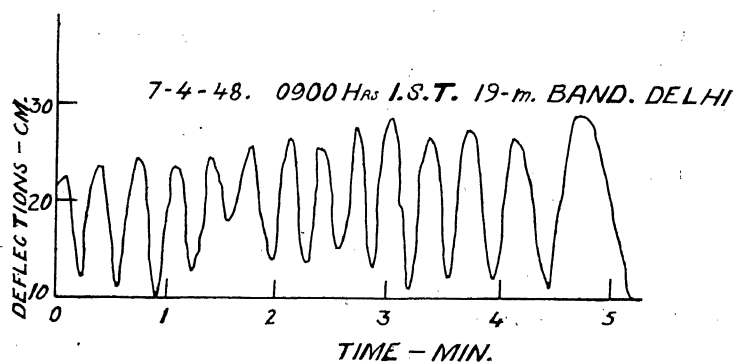


Fig. 4

table. These values may be compared with the minimum electronic densities required for single and double reflections from the  $F_1$  layer for the distance between Banaras and Delhi (678.4 km), which were calculated and found to be  $1.2 \times 10^6$  and  $1.9 \times 10^6$  electrons/cc. respectively. For these calculations, thickness of the ionospheric layer and curvature of the earth have been taken into consideration.

TABLE I.

Figs.	Date.	Time in Hrs. I. S. T.	Wave band.	Type of fading.	Remarks.
1.	23-5-46	1411	19-metre.	Random.	Single reflection From $F_2$ ( $N = 1.6 \times 10^6$ electrons/cc.)
2.	7-5-47	1730	do.	Slow Random.	Double reflection From $F_2$ -layer [ $N = 2.45 \times 10^6$ elec./cc]
3.	21-4-47	1755	do.	Periodic.	Double reflection from $F_2$ -layer [ $N = 1.93 \times 10^6$ elec./cc]
4.	7-4-48	0900	do.	Smooth Periodic.	Single reflection from $F_2$ - [ $N = 1.5 \times 10^6$ elec./cc.]

It will be observed from Figs. 1 and 4 that under suitable conditions single reflections from  $F_2$ -layer may give rise to either random or smooth periodic variation of intensity of the signal. Similarly from Figs. 2 and 3 it will be seen that doubly reflected signals from  $F_2$ -layer will give rise to either slow random or periodic variations from the received signals which may be superimposed on slow random variations. There is, however, a notable difference in the periodic nature of fading between Figs. 3 and 4. The former is due to interference fringes caused by vertical movement of the layer when the electronic density is fairly high and the latter is caused by magneto-ionic splitting of the signal passing through the ionosphere with varying electronic density when it approaches the value corresponding to the maximum usable frequency for the distance between the transmitting and receiving stations. Evidently the period on the former occasion will be usually quick compared to that on the latter occasion as shown in Figs. 3 and 4 respectively.

#### 5. SPACE DIVERSITY RECEPTION.

If there are two receiving aerials separated by a few wavelengths from each other in a horizontal plane, it is possible that they will be acted upon by reflections from two spots in the ionosphere and consequently the variations of intensity in the two aerials will be independent of each other. This principle is made use of in space diversity reception, where the outputs from two or more receivers connected to aerials which are several wavelengths apart from each other, are combined together to obtain a fairly constant strength of the signal received. It may be shown that such independent variations of the signal intensity can be obtained in two vertically-spaced aerials with much smaller separation than that required for horizontally-spaced aerials.

In order to verify the above, two vertical aerials were erected at different heights and separated from each other by about one-third wavelength and were connected to two superheterodyne receivers of equal sensitivities and placed near each other. The receivers were connected to the aerials with transmission lines. Arrangement was

made to observe the intensity of rectified signals in the two receivers as well as their total intensities. The variations of these intensities are shown in Fig. 5. The dotted line represents the variations of intensity in the lower aerial denoted by  $G$  in the diagram, the dash-dotted line shows the variations in the upper aerial denoted by  $E$ , and the continuous line shows the resultant intensity  $T$  obtained experimentally as described above. It will be observed that though there are large variations in the two aerials,  $G$  and  $E$ , their phases are generally opposite to each other and as such the total intensity remains nearly constant.

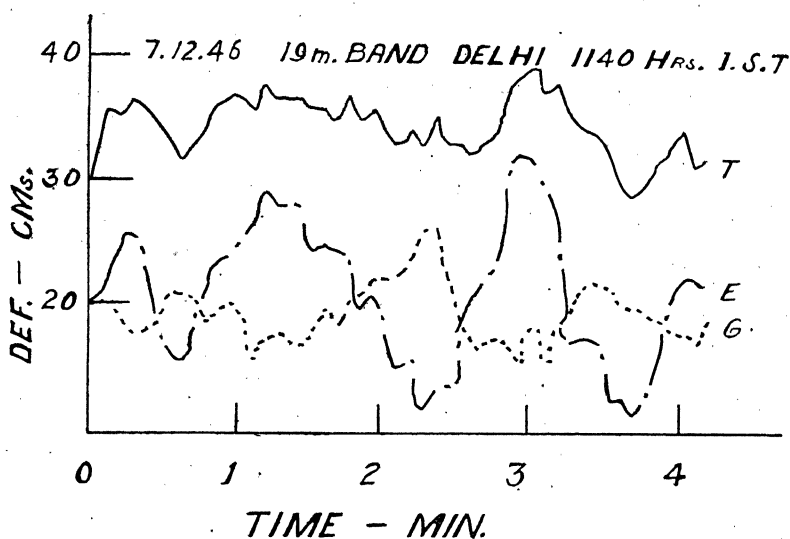


Fig. 5

In order to compare similar variations of intensities in the horizontally spaced aerials, observations were taken with one additional aerial installed at the same level as the upper aerial and situated nearly at the same distance from this, as the lower aerial. This has been shown in Fig. 6, where the dash-dotted and continuous

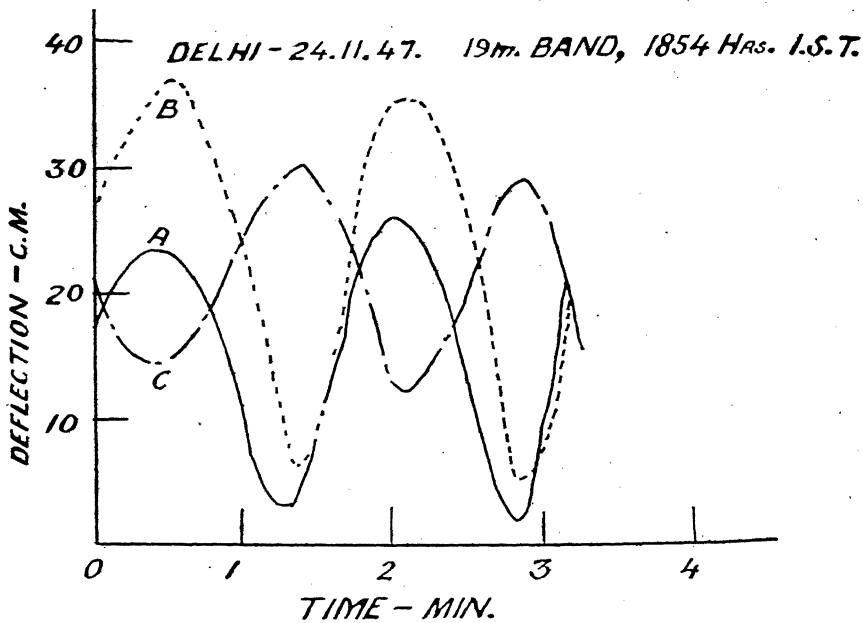


Fig. 6

curves represent the variations of intensity in the lower and upper aerials respectively denoted by *C* and *A* in the diagram, and the dotted curve shows the variations in the horizontally spaced aerial denoted by *B*. It will be observed from this figure that the variations of intensities in the horizontally spaced aerials *A* and *B* are practically in phase with each other, whereas the variations in the vertically spaced aerials *A* and *C*, are generally out of phase. Thus the resultant output from the two vertically spaced aerials will be fairly constant as compared to the combined output from the horizontally spaced aerials.

#### 6. SUMMARY AND CONCLUSIONS.

Various types of fading of shortwave radio-signals have been observed and they have been divided into three main categories, namely (1) random, (2) slow random, and (3) periodic. Visual and automatic records of the above observations have been made and the various types of fading have been explained by assuming random scattering of radio waves from the ionosphere. The first and the

second type of fading have been attributed respectively to single-spot or double and multiple-spot reflections of radio waves from the ionosphere. The third or periodic type of fading has been found to be due to interference fringes caused by either two waves reflected from one or two layers when they possess slow vertical movement or by magneto-ionic split waves, when the electronic density in the ionosphere reaches the value corresponding to the maximum usable frequency for the distance between the transmitter and receiver. Both the above periodic types of fading have been recorded and the conditions of their formation have been verified by the ionospheric data obtained at the time of observations of the fading patterns. Utility of these observations in space-diversity reception has been indicated. A part of this paper was read and discussed in the Indian Science Congress held in Delhi, in January 1947.

In conclusion, the author has great pleasure in recording his thanks to the Research Department, All India Radio, Delhi, for supplying the ionospheric data and to Dr. S. S. Banarjee for his guidance, criticisms and suggestions during the course of the present investigations. His thanks are also due to Prof. G. C. Mukerjee and principal M. M. Sengupta for their helpful interest in the work.

Section of Communication

Engineering & Applied Physics

Banaras Hindu University,

Banaras.

7. 8. 48

*References.*

1. E. V. Appleton and M. A. F. Barnett, *Nature*, 115, 333, 1925.
2. E. V. Appleton, *Journ. Inst. Elec. Eng.*, 66, 872, 1928.
3. J. A. Ratcliffe and J. L. Pawsey, *Proc. Camb. Phil. Soc.*, 29, 301, 1933
4. S. R. Khastgir and A. K. Ray, *Ind. Jour. Phy.* 14, 283, 1940.
5. M. M. Sengupta and S. K. Dutt, *Ind. Jour. Phy.* 15, 447, 1941.
6. S. S. Banerjee and G. C. Mukerjee, *Science and culture*. 11, 571 1946.
7. S. S. Banerjee and G. C. Mukerjee, *Nature*. 155. 15, 1946.
8. E. V. Appleton and W. J. G. Beynon, *Proc. Phy. Soc.* 59, 58, 1947.



**STUDIES IN THE NATURE OF HYDRATED FERRIC OXIDE  
PART II. ADSORPTION OF VARIOUS IONS BY THE  
HYDRATED OXIDE IN ACIDIC, ALKALINE AND  
NEUTRAL MEDIA**

*By*

ARUN K. DEY

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SAUGAR

AND

SATYESHWAR GHOSH

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALLAHABAD

(Read at the meeting on 3rd May, 1948)

**ABSTRACT**

The adsorption of the cations sodium and copper, and that of the anions, chloride, oxalate and ferrocyanide by hydrated ferric oxide has been studied quantitatively. It has been observed that the adsorption of the cations is enhanced when the medium is alkaline, whereas the adsorption is minimum in an acidic medium. On the other hand, the adsorption of anions is pronounced in acidic medium, and the adsorption decreases with the fall in hydrogen ion concentration of the medium. The results have been discussed and the mechanism has been explained on the basis of proton donating or proton accepting capacity of the hydroxide under different conditions.

In Part I of the series<sup>1</sup> we have described our results on the precipitation of hydrated ferric oxide under different conditions of temperature and with varying concentrations of the reactants, ferric chloride and sodium hydroxide solutions. It was observed that the precipitation of hydrated ferric oxide is complete when the amount of sodium hydroxide is about 7 per cent less than the theoretical amount needed. A similar phenomenon has been recorded by Britton<sup>2</sup> in the case of several hydroxides, where he observes that in all the cases of the metal hydroxides investigated, a lesser quantity of hydroxyl ions are able to bring about the separation of metals as insoluble hydrated oxides. In the case of cupric hydroxide the amount of

alkali required to precipitate copper as hydroxide is about 10 per cent less than the theoretical quantity as reported in an earlier communication<sup>3</sup>. This phenomenon has been explained by us on the basis of hydrolytic adsorption of the acid radical, resulting in the liberation of an equivalent quantity of hydroxyl ions, which cause the precipitation of the hydrated oxide.

In the course of our studies on the adsorption by amphoteric oxides, like stannic hydroxide, as we have observed in an earlier paper<sup>4</sup>, the amount of adsorption of ions by an amphoteric oxide is intimately connected with the hydrogen ion concentration of the medium in which the hydrated oxide is suspended. Thus, in the case of hydrated stannic oxide, in the presence of minute quantities of alkali, the adsorption of basic groups like silver ions or the dye methylene blue was pronounced, while in the presence of an acid, the adsorption of ferrocyanide or that of the dye Orange II was prominent.

Since ferric oxide, by virtue of its being able to form ferrites, is of an amphoteric nature, we have in this paper studied quantitatively the adsorption of the basic ions—sodium and copper—and that of acid ions—chloride, ferrocyanide and oxalate—in acidic, neutral and alkaline media.

#### EXPERIMENTAL

Hydrated ferric oxide was prepared by the interaction of equivalent amounts of ferric chloride and sodium hydroxide in aqueous solutions. The reagents were tested for their purity and the sodium hydroxide solution was free from carbonate. The solution of ferric chloride employed was estimated both for iron and chlorine and was found to contain these ions in equivalent quantities. For making the solutions, water free from carbon dioxide was used. The precipitate of ferric hydroxide was washed free from a majority of chlorine ions and finally dialysed till chloride ions were completely removed. The precipitate of the hydrated oxide was then shaken with water in a Jena bottle till a homogeneous suspension was obtained. For all adsorption experiments the freshly prepared suspension of ferric hydroxide containing 0.1358 gram of  $\text{Fe}_2\text{O}_3$  per 25 c. c. was employed.

For determining the amount of a particular ion adsorbed by the oxide, 25 c. c. of the suspension was taken in several 100 c. c. graduated flasks, and measured quantities of the solutions of electrolytes were added. The medium was made acidic or alkaline by adding 1 c. c. of M/100 solutions of either sulphuric acid or sodium hydroxide before raising the volume of the mixture to 100 c. c. The heterogeneous mixture was well shaken and kept immersed in a thermostat at 30° for half an hour. When the hydrated oxide had settled, a measured volume of the clear supernatant liquid was pipetted out and the ion available in the solution determined. Knowing the total amount of the ion present in 100 c. c. of the mixture, the amount of ion associated with the precipitate was found by difference. In the tables below, the ions adsorbed by 0.3158 gram of ferric oxide are expressed in milligram ions in a total volume of 100 c. c. of the mixture.

*Adsorption of Sodium ions from sodium chloride solution*

Sodium in the supernatant liquid was determined by evaporating a measured volume of the liquid to dryness with a drop of hydrochloric acid, heating the residue to constant weight and finally weighing as sodium chloride. The results are given in the following table.

TABLE I

Initial Concentration	Acidic Medium		Neutral Medium		Alkaline Medium	
	Final Concentration	Adsorption	Final Concentration	Adsorption	Final Concentration	Adsorption
20.00	19.56	0.44	19.26	0.74	19.14	0.81
15.00	14.82	0.18	14.34	0.66	14.23	0.77
10.00	9.96	0.04	9.43	0.57	9.33	0.67
5.00	5.00	—	4.56	0.44	4.47	0.53

*Adsorption of cupric ions from cupric sulphate solution*

Copper was estimated in a measured volume of the supernatant liquid by the iodometric method. Since in an alkaline medium there are chances of the removal of copper as hydroxide, the adsorption was measured in acidic and neutral media only. In Table II the experimental results are presented.

TABLE II

Initial Concentration	Acidic Medium		Neutral Medium	
	Final Concentration	Adsorption	Final Concentration	Adsorption
40.00	38.05	1.95	38.05	1.95
30.00	28.35	1.65	28.35	1.65
20.00	18.65	1.35	18.65	1.35
10.00	8.95	1.05	8.95	1.05

*Adsorption of chlorine ions from sodium chloride solution*

In a measured volume of the supernatant liquid, chloride was estimated by titration using standard potassium thiocyanate solution, and ferric alum as indicator. The adsorption of chlorine ions under different conditions are recorded below :—

TABLE III

Initial Concentration	Acidic Medium		Neutral Medium		Alkaline Medium	
	Final Concentration	Adsorption	Final Concentration	Adsorption	Final Concentration	Adsorption
20.00	19.37	0.63	19.38	0.62	19.43	0.57
15.00	14.56	0.44	14.56	0.44	14.60	0.40
10.00	9.75	0.25	9.76	0.25	9.80	0.20
5.00	4.89	0.11	4.90	0.10	5.00	—

*Adsorption of ferrocyanide ions from potassium ferrocyanide solution*

Ferrocyanide was estimated by titration against standard potassium permanganate solution. The change of colour from green to golden yellow marked the end point of the titration. The adsorption of ferrocyanide ions are shown in Table IV.

TABLE IV

Initial Concentration	Acidic Medium		Neutral Medium		Alkaline Medium	
	Final Concentration	Adsorption	Final Concentration	Adsorption	Final Concentration	Adsorption
43.6	42.0	1.6	42.0	1.6	42.5	1.1
32.7	31.5	1.2	31.5	1.2	32.0	0.7
21.8	21.0	0.8	21.0	0.8	21.5	0.3
10.9	10.5	0.4	10.5	0.4	10.9	—

*Adsorption of oxalate ions from potassium oxalate solution*

Oxalate in the supernatant liquid was determined by titration against standard potassium permanganate solution. The amounts of oxalate ions adsorbed are presented in the following table.

TABLE V

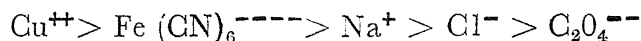
Initial Concentration	Acidic Medium		Neutral Medium		Alkaline Medium	
	Final Concentration	Adsorption	Final Concentration	Adsorption	Final Concentration	Adsorption
80.0	77.5	2.5	78.0	2.0	78.5	1.5
60.0	58.0	2.0	58.5	1.5	59.0	1.0
40.0	38.5	1.5	39.0	1.0	39.5	0.5
20.0	19.0	1.0	19.5	0.5	20.0	—

## DISCUSSION

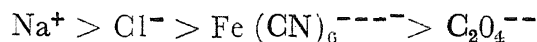
On a perusal of the experimental results presented in tables I to V, it is evident that the extent of adsorption of various ions investigated here, lie in the following order when the adsorption measurements are carried out in an acidic medium:



The order changes in a neutral medium to the following:

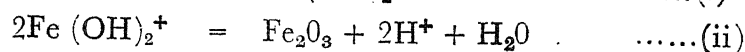
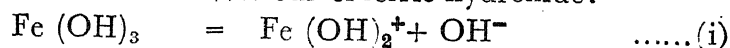


When the medium was made alkaline the order totally changed to:



It may be noted that the change of media from acidic to alkaline totally reverses the order in which the metallic or acidic ions are adsorbed. In an acidic medium, the adsorption of sodium was only 0.44 mgm ions when the initial concentration was 20.00 mgm ions, whereas in an alkaline medium the adsorption increased to 0.86 mgm ions. On the other hand, the acid radicals are preferentially adsorbed in an acidic medium as found from tables III to V.

In part I of the series, we suggested the following scheme to account for the chemical behaviour of ferric hydroxide:



In equation (i) the precipitated ferric hydroxide liberates  $\text{OH}^-$  ions and is, therefore, capable of behaving as a proton acceptor and accounts for the basic nature of ferric hydroxide. Thus, if an excess of hydrogen ions is maintained in the system, the reaction will proceed from left to right and the basic character of the oxide will be more pronounced. Under these circumstances, acid groups like chloride, ferrocyanide and oxalate will naturally be preferentially adsorbed.

Equation (ii) illustrates the acidic behaviour as shown by the liberation of a proton by  $\text{Fe}(\text{OH})_2^+$ . In this case the acid properties of the oxide are prominent, since it behaves as a proton donator. This

is substantiated by the observation that sodium ions are preferentially adsorbed in an alkaline medium, and that the adsorption of sodium diminishes as the acidity of the medium increases.

Therefore, it is evident that since the acid or basic properties of an oxide is dependent on its proton donating or proton accepting capacity, which may be regulated by the hydrogen ion concentration of the medium, the adsorption of cations or anions would naturally vary with the conditions of hydrogen ions of the medium in which the hydrated oxide is suspended.

Further work in this direction, it is hoped, will be able to substantiate the view developed in the present series of papers on hydroxides.

*References*

1. Dey and Ghosh *J. Indian Chem. Soc.*, 1949, 26.
2. Britton *J. Chem. Soc.*, 1925, 2799
3. Dey and Ghosh *J. Indian Chem. Soc.*, 1947, 24, 181
4. Dey and Ghosh *Proc. Nat. Acad. Sci., India*, 1946, 15A, 143

## INSTRUCTIONS TO CONTRIBUTORS

**Articles** should be as *brief* as possible. The viewpoint should be comprehensive in giving the relation of the paper to previous publications of the author or of others and in exhibiting, when practicable, the significance of the work for other branches of science. Elaborate technical details of the work and long tables of data should be avoided, but authors should be precise in making clear the new results and should give some record of the methods and data upon which they are based.

**Manuscripts** should be prepared with a current number of the PROCEEDINGS as a model in matters of form and should be typewritten in duplicate with double spacing, the author retaining one copy. Illustrations should be confined to text-figures of simple character, though more elaborate illustrations may be allowed in special instances to authors willing to pay for their preparation and insertion. Authors are requested to send in all drawings or other illustrations in a state suitable for direct photographic reproduction. They should be drawn on a large scale in Indian ink on Bristol board, with temporary lettering in pencil. Great care should be exercised in selecting only those that are essential. If unsatisfactory drawings are submitted authors may be required to have them redrawn by a professional artist. Particular attention should be given to arranging tabular matter in a simple and concise manner.

**References** to literature, numbered consecutively, will be placed at the end of the article and short footnotes should be avoided. It is suggested that references to periodicals be furnished in some detail and in general in accordance with the standard adopted for the Subject Catalogue of the International Catalogue of Scientific Literature, *viz.*, name of author, with initials following (ordinarily omitting title of paper) abbreviated name of journal, volume, year, inclusive pages.

**Papers** by members of the Academy may be sent to the General Secretary, National Academy of Sciences, India, Allahabad, U.P. Papers by non-members of the Academy should be submitted through some member.

**No papers** exceeding twelve pages of printed matter will be published in the proceedings except with a special permission of the Council.

Every paper must be accompanied by *three copies* of a brief summary not exceeding 300 words in length.

**Proof** will ordinarily be sent and the author is requested to return it with the manuscript at his earliest convenience. All proof corrections involve heavy expenses which would be negligible if the papers are carefully revised by the authors before submission.